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Probing the thermal decomposition process of layered double hydroxides through in situ ^{57}Fe Mössbauer and in situ X-ray diffraction experiments

Daniel X. Gouveia · Odair P. Ferreira · Antonio G. Souza Filho · M. G. da Silva · J. A. C. de Paiva · Oswaldo L. Alves · Josué Mendes Filho

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Abstract The thermal decomposition properties of Mg–Fe hydrotalcites were studied through in situ ^{57}Fe Mössbauer spectroscopy and in situ X-ray diffraction. Abrupt changes in the quadrupolar splitting measured in the Mössbauer spectra revealed a phase transition from the starting lamellar structure to a new crystalline arrangement. By analyzing the Mössbauer parameters we show that the material is highly disordered in the 300–400 °C temperature range. This hypothesis is confirmed by the X-ray results whose diffractograms indicated the collapse of the lamellar structure and the formation of a solid solution.

Introduction

Layered double hydroxides (LDHs) have been widely investigated due to their several applications [1–7]. These lamellar compounds can be viewed as a stacking of positively charged layers formed by an ordered edge-shared octahedral network and of negatively charged layers formed by anions and H_2O molecules. Both anions and the water molecules occupy the interlamellar space in a liquid-like configuration. The general chemical formula of the LDHs can be written as $[M^{II}{}_{1-x}M^{III}{}_{x}(OH)_2](A^{n-})_{x/n}.mH_2O]$ where M^{II} is a bivalent metal ion, M^{III} is trivalent metal ion, A^{n-} is the interlamellar anion. The x value changes from 0.2 to 0.4 [1]. This layered structure leads these materials to be suitable for both sorption and intercalation of anionic species [8, 9].

The LDHs exhibit an interesting property called memory effect. The products resulting from the thermal decomposition experience a spontaneous structural reconstruction when they are placed in an appropriate medium [10–13]. This ability to recover the initial structure opened up many possibilities for applying these compounds in environmental related applications. The greatest advantage of using these materials is the possibility of recycling them after their usage because they reconstruct [14, 15]. In this scenario, it is of great interest understand the thermal decomposition process step by step in order to model and improve the efficiency of the reconstruction phenomena.

The structural changes during the thermal treatment of LDHs have been widely investigated [16–21]. However, the precise information about the structural changes during thermal decomposition would be achieved if one employs local probing techniques since some of the phases are disordered. Thus, techniques such as Mössbauer, NMR and XAS are very powerful for performing such studies. Both ^{27}Al MAS NMR and XAS have been used to investigate the Al-based LDHs [16–19]. LDHs containing trivalent iron have been

D. X. Gouveia · A. G. Souza Filho (✉) ·
M. G. daSilva · J. A. C. de Paiva · J. M. Filho
Departamento de Física, Universidade Federal do Ceará,
P.O.Box 6030, 60455-900 Fortaleza, CE, Brazil
e-mail: agsf@fisica.ufc.br

D. X. Gouveia
Centro Federal de Educação Tecnológica-CEFET,
Fortaleza, CE 60040-531, Brazil

O. P. Ferreira · O. L. Alves
LQES – Laboratório de Química do Estado Sólido,
Instituto de Química, UNICAMP, P.O. Box 6154, 13084-862
Campinas, SP, Brazil

reported as an efficient system for applications in sorption and catalysis [22, 23]. For this specific system, ^{57}Fe Mössbauer spectroscopy is a very appropriate tool for studying the chemical environment of the Fe and for learning more about the chemical and structural properties of this system [24, 25]. Additionally, the best approach for studying the local order changes during the decomposition process is through in situ experiments. The goal of this paper is to study the thermal decomposition process of Mg–Fe based layered double hydroxide through in situ Mössbauer spectroscopy and in situ X-ray diffraction experiments.

Materials and methods

All chemicals (reagent grade, Ecibra) were used as received, without previous purification.

The LDHs were synthesized by the co-precipitation method. An aqueous solution (70 mL) containing 0.1 mol of $Mg(NO_3)_2\cdot 6H_2O$ and 0.025 mol of $Fe(NO_3)_3\cdot 9H_2O$ (Mg/Fe = 4) was added dropwise under vigorous mechanical stirring into 150 mL of NaOH (2.0 mol/L) and Na_2CO_3 (0.1 mol/L). During the synthesis, the temperature was kept at 45 ± 3 °C. When addition of the nitrates was completed, a thick slurry was obtained, and heated for 2 h at 85 ± 3 °C for ageing. The obtained products were isolated by filtration and washed several times with deionized water until pH 7–8. Afterwards, the solids were dried at 60 °C for 24 h.

Chemical analysis for Mg and Fe were carried out by ICP-OES (Perkin-Elmer spectrometer, model Optima 3000DV) after the dissolution of the sample in 0.1 mol/L HCl.

In situ X-ray diffraction experiments were carrying out in the range of 30–600 °C in air by using a Shimadzu XRD6000 diffractometer equipped with a high temperature furnace (HA1001, Shimadzu). A 5 °C/min temperature rate and a temperature holding time of 15 min before each measurement were used. CuKα ($\lambda = 1.5406$ Å) radiation operating with 30 mA and 40 kV and a scan rate of 1 °/min was employed.

The Mössbauer experiments were performed on powdered samples by using a constant acceleration spectrometer with a radioactive source of ^{57}Co within an Rh host. The spectral analyses were performed by using the Normos fitting routine, which makes use of a set of Lorentzians and computes the contribution of each curve to the total absorption spectrum through the least-squares procedure. All the Isomer shifts (δ) quoted in this paper are relative to metallic iron (α-Fe). The in situ Mössbauer experiments were carried out using an open homemade furnace coupled to a temperature controller (Eurotherm) with a temperature control of ±2 °C. A holding time of 15 min was employed to stabilize the temperature samples before each measurement.

The differential thermal analysis (DTA) experiments were performed by using a Shimadzu instrument (model 50WS). The measurements were carried out using 40 mg of sample under static air and a heating rate of 5 °C/min.

Results and discussion

The chemical analysis for Mg and Fe showed a Mg/Fe molar ratio equal to 3.74 ($x = 0.21$). This result indicates that the co-precipitation step was efficiently carried out.

The DTA curve for Mg–Fe sample is shown in Fig. 1. It was observed two endothermal peaks located at about 190 and 350 °C. The first thermal event is attributed to the loss of interlamellar water (without the collapse of the layered structure) along with a grafting process of the interlamellar anion as we will discuss later on. The second thermal event (at 350 °C) is related to the collapse of the lamellar structure where both hydroxyl groups and interlamellar anions are released. The results are qualitatively consistent with those observed for other hydrotalcite systems [26–28].

The X-ray diffractogram taken at 30 °C [see lower trace in Fig. 2] has the signature of a typical layered structure well-known in the literature [JCPDS 25-0521]. The diffractogram indicates a good crystallinity of the sample and the peaks can be indexed to a

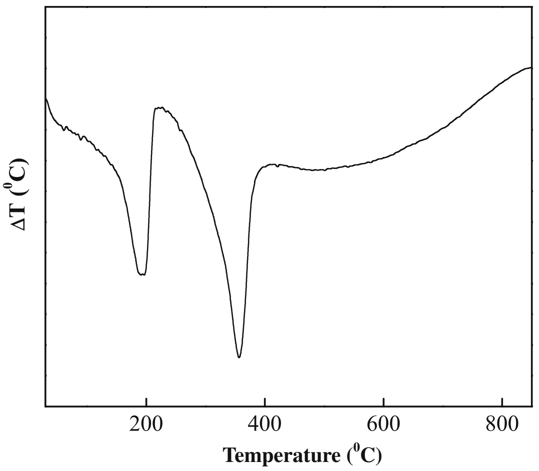

Fig. 1 DTA curve for Mg–Fe layered double hydroxide

rhombohedral structure belonging to the space group R$\bar{3}$m. The *a* and *c* cell parameters are 3.10 and 23.25 Å, respectively. This *c* value is typical of hydrotalcite containing carbonate anions in the interlamellar space. The diffraction peaks present a linewidth typical of nanocrystallites. The average crystallite size was evaluated (considering the (003) and (006) Bragg peaks) through Scherrer's equation, $L = \kappa\lambda/\beta\cos\theta$. We assume $\kappa = 0.9$ (spherical shape) and found the crystallite size to be about 31 nm.

Upon increasing the temperature from 30 to 100 °C we did not observe any significant change in the diffractograms (see Fig. 2), thus indicating that up to 100 °C the lamellar structure remains intact. However, in the 175–250 °C temperature range, drastic changes were observed in the X-ray patterns . Firstly, the peak (003) exhibits an abrupt shift towards higher 2θ values. This phenomenon has been attributed to a contraction of the interlayer distance due to a grafting process where the carbonate anions attach to the layers. This hypothesis has been confirmed in Mg–Fe LHDs by infrared spectroscopy. It was observed a splitting of the vibrational modes indicating a symmetry lowering effect of the carbonate anions [29]. A similar effect has been observed in other LDHs systems [30, 31]. Secondly, the other X-ray peaks get broadened and also change their angular positions. The results suggest after the grafting process the lamellar structure is still preserved but the crystalline structure is different. The temperature dependence of the *a* and *c* cell parameters are shown in the inset to Fig. 2. The *c* versus temperature data clearly indicate the contraction of the lamellar distance between 170 and 250 °C. By further increasing the temperature, the LDH exhibits a progressive broadening of the X-ray peaks, thus indicating an increasing disorder in the crystalline structure. The X-ray pattern observed at 350 °C is typical of a highly disordered system and at this temperature the X-ray data clearly show that the lamellar structure has been destroyed. Above 350 °C the peaks observed could be assigned to MgO (JCPDS 45-0946). However, the excessive broadening of the peaks and slight changes in their 2θ positions suggest that the thermal decomposition leads to the formation of a solid solution and not isolated oxide phases. The Mössbauer data support these two structural changes observed in the X-ray measurements, as discussed next.

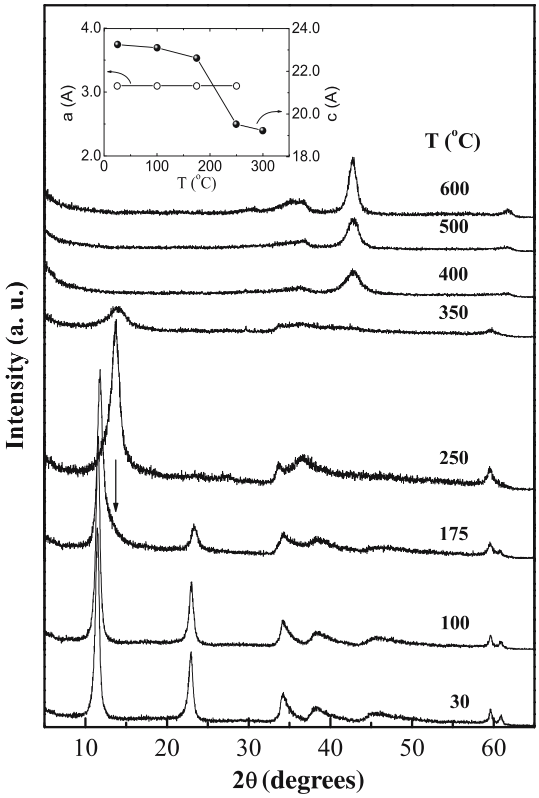

Fig. 2 In situ X-ray diffractograms recorded during the thermal decomposition process of a Mg–Fe layered double hydroxide. The inset depicts the temperature dependence of the cell parameters

We show in situ Mössbauer spectra for several temperatures in Fig. 3. The lower trace in Fig. 3 shows the Mössbauer spectrum of the as-prepared LDH. The Isomer Shift δ and the Quadrupole splitting Δ values clearly indicate that the iron is in the high spin Fe^{3+}state with octahedral coordination. We have

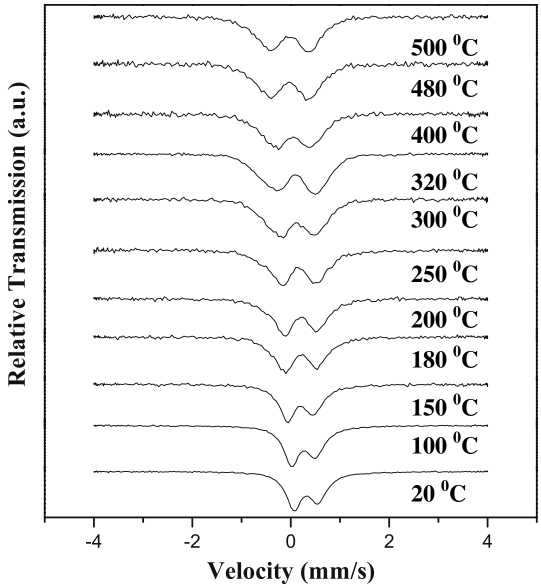

Fig. 3 In situ ^{57}Fe Mössbauer spectrograms obtained during the thermal decomposition process of a Mg–Fe layered double hydroxide

performed the experiments in the normal incidence and in the magic angle configuration (not show here). The results revealed that our samples are free of texture effects. Thus this asymmetry observed in the Mössbauer spectra should be related to spin-lattice relaxation mechanisms [32, 33].

In the 20–500 °C temperature range, the Mössbauer spectra exhibit a doublet structure and the Fe^{3+} configuration throughout this range. It is clear that the center of the doublet (Isomer shift) is temperature-dependent, i.e., it decreases as the temperature increases. This effect is well known as the second order Döppler shift [33]. The main changes observed in the Mössbauer spectra can be followed in detail by analyzing the Mössbauer parameters (Isomer shift, Quadrupole splitting, and linewidth) versus temperature plots. The results are shown in Fig. 4 and tell us precisely the temperature dependence of the parameters. No anomalies have been observed in the Isomer shift behavior (see Fig. 4a) thus indicating that the Fe coordination does not change with temperature. This is not the case for quadrupolar splitting (see Fig. 4b), for which two events are clearly identified. At about 180 °C an abrupt change is observed in the Δ versus T plot. This change coincides with the first endothermal peak observed in the DTA curve and it is attributed to the phase transition the LDH experience when the grafting process takes place. We discussed this issue in the in situ X-ray results. The interlayer anion attachment event to the layers induces a modification of the local electric field gradient on the Fe^{3+} site and this effect in turn, modifies the quadrupolar splitting values. The second clear change in the quadrupolar splitting plot is observed in the 300–350 °C temperature range, where the values are predominantly high. This behavior indicates that, in this temperature range, a remarkable disorder effect is taking place in the LDH structure. The temperature range agrees well with the second endothermal peak observed in the DTA scan. The high degree of disorder also coincides with the collapse of the layers, where the samples present X-ray diffractograms typical of a highly disordered material (amorphous phase). Therefore, by combining X-ray (long range order probe) with Mössbauer data (short range order probe) we can conclude that the products of the thermal decomposition process are amorphous in the 300–400 °C temperature range. By combining in situ X-ray diffraction and in situ Mossbauer spectroscopy is a very good approach to monitor the thermal decomposition process step by step.

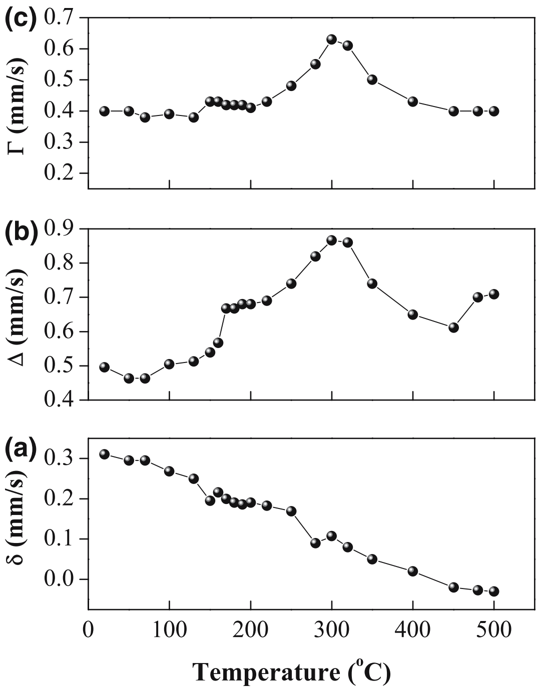

Fig. 4 Temperature dependence of the Mössbauer parameters obtained from in situ experiments. (**a**), (**b**) and (**c**) show the Isomer shift (δ), the Quadrupolar splitting (Δ) and the Linewidth (Γ), respectively

Conclusions

In summary, we have studied the thermal decomposition of Mg–Fe based LDH through in situ ^{57}Fe Mössbauer and in situ X-ray diffraction experiments. We have observed from the X-ray data that an interlamellar contraction occurs at about 175 °C and the collapse of the lamellar structure occurs at about 350 °C. The analysis of Mössbauer parameters allowed us to detect the structural changes the LDH have experienced. The higher values observed for quadrupolar splitting of the Mössbauer spectra indicate that the chemical environment in the 300–350 °C temperature range is highly disordered. These results point out to the formation of a solid solution instead of a mixture of oxide phases.

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